

FARM FIELDS AND RESIDENTIAL YARDS SAMPLING AND ANALYSIS PLAN

**Tannery Sludge Farm Fields
Andrew, Buchanan, Clinton and DeKalb Counties**



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1.0 INTRODUCTION

As authorized under the federal Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986, the Missouri Department of Natural Resources (Department), Hazardous Waste Program (HWP), Site Assessment Unit is conducting Pre-CERCLIS Site Screenings on selected farm fields in Andrew, Buchanan, Clinton and DeKalb Counties where tannery sludge has been applied as a fertilizer.

The purpose of this investigation is to determine whether application of tannery sludge to farm fields as fertilizer has resulted in unacceptable risk to residents living in close proximity to those fields.

2.0 SITE INFORMATION

2.1 Location

The Tannery Sludge Farm Fields are agricultural fields in various locations in Andrew, Buchanan, Clinton and DeKalb Counties in northwestern Missouri, where tannery sludge has been applied as a fertilizer. Figure 1 shows the overall 4-county area where tannery sludge was applied.

2.2 History/Previous Investigation

Starting in 1983 Blueside, which became Prime Tanning in 1996 and was then purchased by National Beef Leathers (NBL) in March 2009, land applied sludge from its tanning process as an agricultural fertilizer. The sludge was provided free to farmers in Andrew, Buchanan, Clinton and DeKalb Counties. NBL is located at 205 Florence Road in St. Joseph, Missouri. Tannery records provided by NBL indicate that the sludge was delivered to 111 locations in the four County area covering over 56,000 acres of agricultural fields. Sludge was land-applied with a mechanical spreader, and most applications were performed by one individual. The sludge was applied over a period of 26 years, ending in the spring of 2009 when concerns were raised regarding the hexavalent chromium (Cr^{6+}) content of the sludge and potential risks posed to farmers working the land and to residents living adjacent to application areas. MDNR file information indicates the applications were initially

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conducted under a letter of approval from the Department and, later, under Department-issued permits until 2005, at which time, permits were no longer required.

2.2.1 April/May 2009 MDNR Sampling Event

An initial sampling event took place over two mobilizations by MDNR on April 29, and May 1, 2009 (MDNR 2009f). The scope of that investigation included the collection of agricultural field surface soil, stockpiled material at NBL, sludge, surface water, and groundwater samples to assess for the presence and levels of Cr₆₊, in addition to other constituents typically associated with tanning operations. Initial efforts focused upon process wastes at the facility itself with limited surface soil sampling at selected farm fields.

Based on the sample results, it was determined that hexavalent chromium (Cr₆₊) was the primary contaminant of concern. No Cr₆₊ was detected in surface water collected near the NBL facility or in groundwater samples collected from NBL facility wells and a nearby residential well. Samples of sludge from various points in the tanning process contained Cr₆₊ concentrations between 1.7 mg/kg and 46 mg/kg. Seven soil samples were collected from farm fields that had received sludge, and one background soil sample from a field that did not. Concentrations of Cr₆₊ ranging between non-detect and 49 mg/kg were observed. However, all non-aqueous samples were analyzed using a colorimetric method (EPA SW846-7196A), which is susceptible to interferences. Also, duplicate sample results did not agree well with each other indicating poor overall sampling precision.

2.2.2 May 2009 Keystone Pipeline Sampling Event

In May 2009, Transcanada Keystone Pipeline, LP conducted soil sampling in cultivated areas traversed by its pipeline in Caldwell, Clinton and Buchanan Counties (Hackman, 2009). Approximately 260 surface soil grab samples were collected, 5 of which were located in areas that received tannery sludge applications. Hexavalent chromium was detected in seven of the samples at concentrations ranging between 0.54 mg/kg and 2.7 mg/kg. Five of the seven detections occurred in Clinton County, one in Buchanan County, and one in Caldwell County. None of the Cr₆₊ detections occurred in samples collected from areas known to have received sludge applications. The detection level reported by the laboratory was approximately 0.50 mg/kg.

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2.2.3 Saint Joseph Sanitary Landfill May 2009 Sampling Event

Sampling was conducted by MDNR on May 21, 2009 in portions of the Saint Joseph Sanitary Landfill that had received tannery sludge waste between 1981 and present (MDNR, 2009b, MDNR, 2009c). The tannery waste was disposed of in two designated areas within the landfill initially, and then was co-disposed with municipal solid waste thereafter. Sludge sampling was conducted from various depths at 8 locations from within the two designated areas.

Sludge samples were analyzed for total chromium by EPA Method 6010B, and for Cr⁶⁺ by EPA Method 7196A. Total chromium was detected in all of the samples at concentrations ranging from 15.5 mg/kg to 20,600 mg/kg, with a mean of 11,000 and a median of 15,000. In about half of the samples, Cr⁶⁺ was reported below the detection level (<0.1mg/kg to <3.9mg/kg). In those samples where Cr⁶⁺ was detected, the maximum concentration was 29mg/kg, and the low was 0.8mg/kg. The ratio of Cr^{6+:}Cr ranged from a high of 21% to a low of 0.003%, with a mean of 13.7% and a median of 0.03%

2.2.4 August 2009 MDNR Sampling Event

On August 12, 2009, MDNR conducted a soil sampling event in one selected agricultural field (MDNR, 2009d, MDNR, 2010). The purpose of the event was to determine how well the variability of total Cr (analyzed by XRF) correlated to the variability of Cr⁶⁺ (analyzed by the lab) across different spatial scales in the agricultural field soils. If the variability of total Cr XRF data was similar to or greater than the Cr⁶⁺ variability, it would indicate that the XRF could be used in the field as a real-time analytical tool to provide a conservative estimate of Cr⁶⁺ variability based on total Cr results. This information will be used in the field to determine how many incremental samples to collect and how many increments to collect per sample.

Three small variogram plots were established in different areas across an agricultural field that had received sludge in early 2009. Ten surface soil samples were collected from different spatial scales within each plot, dried, crushed, sieved and analyzed for total Cr by XRF and for Cr⁶⁺ by EPA SW-846 Method 7199. Statistical analysis showed that the variability of total Cr analyzed by XRF across

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various spatial scales was generally greater than Cr⁶⁺ variability, thus making the use of XRF a viable field analytical method for use in sampling of the agricultural fields. Both the total Cr XRF and laboratory Cr⁶⁺ data showed low variability across the spatial scales within the variograms. This data indicated that during full implementation of the farm fields sampling, the contaminant variability could be controlled by sampling within larger 1-acre sampling units.

2.2.5 October 2009 MDNR Sampling Event

Results from the August 2009 sampling event indicate that Cr⁶⁺ laboratory method will provide the data needed for the agricultural fields' assessments. However, due to the lower risk-based screening level for residential yards vs. agricultural fields (2 mg/kg vs. 86 mg/kg), the method required modification before use on residential yards. Specifically, a lower detection level was needed, and measures were required to improve subsampling precision. Further, due to sensitivity limitations of the XRF for total Cr, use of the XRF for guiding incremental sampling design in residential yards would not be practical.

A residential yard pilot study was conducted in October 2009 (MDNR, 2009a, MDNR 2010). The goals of the study were to determine the sensitivity requirements needed for laboratory Cr⁶⁺ analyses on yard soil samples, evaluate the influence of laboratory subsampling methods on data uncertainty, and to determine the most conservative generic incremental sampling design to apply to the residential yards.

3.0 DATA QUALITY OBJECTIVES

To help ensure precise, accurate, representative, complete, and comparable data are achieved, all field work and analyses will be conducted in accordance with the Quality Assurance Project Plan (QAPP) for Pre-Remedial Site Assessment/Pre-Removal and Targeted Brownfields Site Assessments Revision 6, December 7, 2007, and ongoing. The QAPP describes the general data quality objectives for site assessment investigations conducted by the HWP and ESP. Those data quality objectives specific to this project are described below.

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3.1 Problem Statement

Leather tannery waste sludge has been land-applied as fertilizer on over 56,000 acres of agricultural fields in four counties of northwest Missouri. The sludge was applied over a period of 26 years, ending in the spring of 2009. There is concern regarding the Cr₆₊ content of the sludge and potential risks posed to residents living adjacent to application areas.

3.2 Planning Team

The planning team for this sampling event includes various project managers in HWP and the Environmental Services Program (ESP), and chemists in the ESP Chemical Analysis Section (CAS) as described in the QAPP. Additional planning team members include Jonathan Garoutte and other staff at the Department of Health and Senior Services (DHSS), Kelly Schumacher, Sue Casteel, Don Lininger and Ron King with EPA Region 7, Deana Crumbling with the EPA Technology Innovation Field Services Division, Rob Tisdale, Tetra Tech EMI, and Ben Wozniak, Project Manager with Applied Speciation Laboratories.

3.3 Conceptual Site Model

Waste sludge from various leather tannery operations was offered as fertilizer to farmers over a 4-county area in northwest Missouri. The sludge contained high levels of organic carbon, phosphorous and nitrogen as well as residual levels of total chromium and potentially other agents used in the tanning process. Sampling of the sludge conducted at the tannery facility in April/May revealed unexpected levels of chromium in the oxidized form, Cr₆₊ which is a carcinogen and could pose a potential health threat.

The tannery has provided MDNR and EPA with detailed records describing which fields received sludge, when applications occurred, the mass of sludge applied per acre, total chromium concentrations (not Cr₆₊ however), and total Cr applied per acre. The records indicate that the concentration of total Cr in the sludge has varied over the years, with older sludge generally containing higher levels than more recently generated sludge. Certain fields received higher masses of sludge per application, more applications, and more frequent applications.

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The sludge was delivered to farm fields and either loaded directly into a mechanized spreader for distribution over the fields, or stockpiled on the ground for subsequent distribution. The applications were nearly all done by one individual working for the tannery. This individual is believed to have applied the sludge in a fairly uniform manner, and to have buffered (not applied) near streams, drainage areas, residences, tree lines. As the applied sludge was exposed to the weather, one would expect some runoff and concentration of chromium in lower elevation areas. One would also expect to see higher, potentially more heterogeneous chromium levels near where the sludge was loaded onto the spreader or staged prior to loading. Areas where the spreader turned corners might also be expected to be more heterogeneous. Higher Cr₆₊ levels would be expected in portions of the fields and yards where soil conditions are more conducive to oxidation of Cr₃₊ to Cr₆₊. Soils with lower organic carbon content and higher pH, could be expected to have higher ratios of Cr_{6+:} Cr₃₊. Cr₆₊ concentrations in residential yards should decrease relative to concentrations in the nearest sludge-applied field with distance from that field. A fairly uniform distribution of Cr₆₊ concentration would be expected across the residential yards due to the nature of wind deposition. However, heterogeneous areas are possible due to wind break features, localized wind pattern effects, and predominant wind directions.

The primary exposure route of concern for the residential yards is ingestion/inhalation of Cr₆₊ – containing soil and dust that comes to be located in residential yards due to wind deposition from the sludge-applied fields. Based on this exposure scenario, soil at the surface or near the surface (0-2") will be of primary interest since that is the fraction most easily mobilized by wind. The smaller particle sizes will be of interest since they are the most likely to be transported thru wind deposition, and to be accessed through direct contact in the yards. A less probable route of exposure is transport of Cr₆₊ vertically through the soil column into groundwater, and ingestion of groundwater by residents with private wells. Sampling will be conducted to assess both of these potential exposure routes as part of this investigation.

Other possible sources of Cr₆₊ in rural agricultural yard and field soils include the following:

- background levels present in the native soils;

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- cement dust;
- wood preservative chemicals and/or preserved wood;
- paints/pigments;
- chromium-based catalytic converters and asbestos linings and road dust containing these materials; and
- antifreeze.

3.4 Resources, Constraints and Deadlines

The project will be funded through the Superfund Consolidated Cooperative Agreement with the USEPA.

3.5 Study Questions

The two principal study questions are:

- What is the background concentration of Cr₆₊ in the groundwater and in surface soil of agricultural fields and residential yards unaffected by tannery sludge in the site area (background concentrations)?
- Does the average Cr₆₊ concentration in the groundwater and surface soil of the farm fields or residential yards in sludge-applied areas exceed background and/or risk-based soil screening levels?

3.6 Inputs Into The Study Questions

The following lists the primary inputs required to address the principal study questions.

Risk-based screening levels for Cr₆₊ (EPA, 2009, DHSS, 2009):

- 0.3 ug/L in residential drinking water wells;
- 86 mg/kg in agricultural farm fields; and
- 2.0 mg/kg in residential yard surface soil.

The risk-based screening level for the farm fields was based on an exposure scenario of ingestion/inhalation of contaminated soil by farmers working in the sludge-applied fields,

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transportation of windborne sludge-contaminated soil to nearby residences, and subsequent inhalation by sensitive members of the population (DHSS, 2009). The assumption was made that sludge application occurred across an average farm field size of 80 acres. Although risk to farmers working in the fields was considered, the screening levels were driven primarily by risk to child residents living adjacent to sludge-applied fields. The screening level therefore represents a maximum average concentration of Cr₆₊ across an 80-acre farm field that if present, would not result in an unacceptable risk to farm workers or residents living nearby.

The screening level developed for residential yard surface soil was based on direct exposure (ingestion and inhalation) by residents to Cr₆₊ contaminated soil across the entire yard. The yard screening level therefore represents the maximum average concentration of Cr₆₊ in surface soil across a residential yard that, if present would not pose an unacceptable risk. The screening level developed for residential drinking water was based on the typical exposure assumptions from the EPA Risk Assessment Guidance for Superfund (RAGS), and using the same toxicity values and risk level used to develop the soil screening levels.

The representative concentration of Cr₆₊ :

- In drinking water wells at residences in areas not near sludge-applied farm fields (background levels);
- In drinking water wells at residences adjacent to sludge-applied farm fields;
- In surface soil (0-2") of sampling units and decision units established in sludge-applied farm fields and residential yards near those fields;
- In surface soil of sampling units and decision units established in farm fields and residential yards in areas unaffected by sludge application (background levels).

The background Cr₆₊ level in groundwater will be determined by averaging the results from 3 background well locations. Any non-detect results will be set to the laboratory's reporting level for purposes of calculating an average. Target well Cr₆₊ concentrations \geq 3 times the background average will be considered significantly above the background concentration.

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Background Cr₆₊ level in residential and farm field soils will be determined from data collected in the same manner as the sludge-applied farm fields and nearby residential yards. Background concentration limits (BCLs) will be calculated as the 95% upper prediction limit (UPL) using the USEPA ProUCL statistical software program (USEPA, 2009a). Target farm field or yard DU Cr₆₊ concentrations exceeding the BCL will be considered to be significantly above the background concentration.

3.7 Study Boundaries

The entire site includes all sludge-applied fields and adjacent residential properties across the 4-county area (Figure 1). Since it is not feasible to sample the entire site, an initial study area was selected in which to conduct sampling. EPA R7 staff selected a subset of sludge-applied fields for assessment from the extensive records of application dates, volumes and locations provided by NBL. The subset includes 15 parcels that represent relatively high, medium and low rates of sludge application and frequency, and include fields that received more recent and historic applications. An effort was made to include fields in all four counties. Sampling results from these 15 fields will be used to assess risk and to determine whether sampling at additional fields is needed. Residential yards and wells adjacent to or nearby these 15 parcels will also be sampled. Background soil sampling locations have also been selected in each of the four counties. Figure 1 also shows the locations of the 15 farm fields, residences, and background sample locations.

Temporal boundaries on the study were established based on the planting and harvesting seasons. In order to avoid interfering with these activities, sampling in the farm fields will need to be conducted between the months of December and March.

3.8 Decision Rules

- If the average Cr₆₊ concentration in the surface soil of the farm fields or residential yards is above the background concentration level (BCL), they will be compared to risk based screening levels to assess potential risk. Otherwise we will conclude that

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tannery sludge application has not resulted in elevation of Cr6+ concentrations above background levels.

- If the average Cr6+ concentration in the fields or yards is above the BCL and exceeds the risk-based screening level, we will recommend additional farm- or residence-specific risk assessment, additional sampling activities, and/or remedial action. Otherwise we will conclude that tannery sludge application has not resulted in Cr6+ levels that pose an unacceptable risk.
- If the Cr6+ concentration in residential wells exceeds the BCL, they will be compared to risk based screening level to assess potential risk. Otherwise we will conclude that tannery sludge application has not resulted in elevation of Cr6+ concentrations in groundwater above background levels.
- If the Cr6+ concentration in residential wells exceeds the BCL and the risk-based screening level, we will recommend additional residence-specific risk assessment, sampling activities, and/or remedial action, otherwise we will conclude that tannery sludge application has not resulted in unacceptable impacts to groundwater.

3.9 Tolerable Limits on Decision Error

Our hypothesis is that the farm fields and residential yards are contaminated with Cr6+ at above the screening levels. Falsely rejecting that hypothesis, considered a Type I error, would mean mistakenly concluding that a contaminated yard or farm field is clean. Falsely accepting this hypothesis, considered the Type II error, would mean concluding that a yard or field is contaminated, when in fact it is clean. The Type I error is considered more serious since it would result in farmers and residents unknowingly being exposed to unacceptable levels of contamination. The probability of making a Type I error (α) is therefore set to 0.05. In other words, we plan to correctly identify actually contaminated DUs 95% of the time. The Type II error limit (β) is set at 0.10, meaning that we are willing to tolerate mistakenly concluding that a clean DU is contaminated up to 10% of the time.

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3.10 Sampling Design

Results from pilot studies conducted in August and October 2009 were used to develop sampling designs for the farm fields and residential yards. The designs are discussed in general in the sections below, and further detailed in Section 4.

3.10.1 Farm Fields

Since it is not feasible to sample the entire sludge-applied areas within all of the 15 farm fields selected for the study, a statistical sampling approach was developed to identify and sample subareas within the fields in a way that allow for MDNR to confidently make conclusions about the average Cr₆₊ concentrations across the entire fields. The approach will use a combination of in-situ real-time XRF analyses and laboratory analyses, and will use a tiered incremental sampling approach. Using incremental sampling with the proper spacing and number of increments provides a better estimate of the true average Cr₆₊ over the DU than a discrete sampling design that is forced to reduce sampling density because of analytical costs. An incremental strategy has the benefit of significantly reducing total analytical costs, while actually increasing the sampling density and thus the representativeness of data for supporting determination of the DU's Cr₆₊ average concentration.

The sludge-applied portion of each selected farm field will be considered a decision unit (DU). This is the area over which we want to determine the average Cr₆₊ concentration. If the sludge-applied area is significantly greater than the exposure unit used to develop the screening level (80 acres), the field will be divided into two or more equally sized DUs. No DU will exceed 100 acres. One-acre SUs will be selected from within the DU for sampling. Initially, three one-acre sampling units (SUs) will be identified for sampling in the field using visual observations and the CSM assumptions stated in Section 3.3. Since the variability of chromium concentration within and between the 3 SUs will be used to determine the density of increments to be collected within the SUs and the number of SUs to

Definitions:

Decision Unit (DU) = exposure unit. For farm fields, the DU \leq 80 acres; no larger than the exposure unit used to develop the screening level. For the residential yards, the DU is the entire yard.

Sampling Unit (SU) = 1- acre blocks for farm fields, or areas designated within each residential yard for collection of an incremental sample.

Incremental Sample (IS) = sample formed by systematically combining equal-mass increments of soil together to create a sample that represents the entire SU.

Tiered IS = incremental samples formed by combining together equal-mass aliquots from other incremental samples to create a sample that represents an entire DU.

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be sampled for Cr₆₊ analyses, the most conservative approach is to try and identify SUs with the greatest within-SU and between-SU Cr₆₊ variability. We will look for areas within the DU where sludge could have been applied unevenly such as mechanical spreader turning areas, loading/stockpiling areas, and obstacles in fields (clumps of trees, rock piles, "necks" between streams). We will also look for areas where sludge would be expected to be evenly applied such as in the middle of long stretches of open ground. Other factors to be considered in SU selection include surface elevation, visual clues (color of soil, presence of actual sludge, crop growth, vegetation color), and farmer-provided information.

XRF analyses of discrete soil samples will be used to assess the variability of total chromium in surface soils within the SUs, and that information will be statistically evaluated to determine the number of SUs to sample within the DU, and the number of increments of soil to include in each SU. The assumption that total chromium variability would serve as a conservative surrogate for Cr₆₊ variability was tested and verified during the farm fields' pilot sampling event. Incremental samples will then be collected from within the SUs for Cr₆₊ analyses. Regardless of the in-situ XRF results, a minimum of 10 increments will be collected per SU, and a minimum of 5 SUs will be sampled per DU. A portion of each SU incremental sample (SUIS) will be pooled together to form a second tier IS sample that represents the entire DU (DUIS). Both the SUIS and DUIS samples will be submitted for laboratory analysis of Cr₆₊. One SU in half of the DUs sampled will be sampled in triplicate to assess the overall sampling precision.

The SUIS Cr₆₊ results will be used to calculate a 95% UCL on the mean, which will be compared to the BCL and the screening level. The DUIS Cr₆₊ result should lie within a 95% confidence interval established using the SUIS Cr₆₊ results. If it does so consistently across the various DUs, it may be defensible to modify the sampling design for any future expanded sampling events by reducing the number of SUIS samples submitted for Cr₆₊ analysis, and relying instead on the DUIS Cr₆₊ result to represent the mean DU concentration.

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Results of the XRF analyses will be evaluated as the project develops, and as Cr₆₊ results become available. If it is determined that the XRF analyses are not providing valuable information to guide Cr₆₊ sample collection, it may be scaled back or eliminated. This may occur for example if it is observed that the variability of total Cr is very low both within and between the farm field SUs, such that statistical analysis of the XRF data always results in defaulting back to the minimum number of increments (10) and SUs (5) to be sampled for Cr₆₊ analyses.

3.10.2 Residential Yards

The entire residential yard will be considered the decision unit. Professional judgment and visual cues will be used to divide the DU into several non-overlapping sampling units (SUs). Divisions will be based on likely differences in exposure potential, Cr₆₊ concentration and variability, and other possible observed parameters. A minimum of 3 SUs will be selected at each residence. Due to sensitivity limitations of XRF, no real-time measurements will be used for the yards. Instead, based on results from the yard pilot study, an incremental sample will be collected from within each SU. The number of increments to be collected per SU will be determined using results from the pilot study (not yet available). A portion of each SUIIS samples will be combined to form a second tier DUIS sample. All SUIIS and DUIS samples will be submitted for Cr₆₊ laboratory analysis. One SU will be sampled in triplicate at each DU to assess overall sampling precision.

The SUIIS Cr₆₊ results will be used to calculate a 95% UCL on the mean, which will be compared to the BCL and the screening level. The DUIS Cr₆₊ result should lie within a 95% confidence interval established using the SUIIS Cr₆₊ results. If it does so consistently across the various DUs, it may be defensible to modify the sampling design for any future expanded sampling events by reducing the number of SUIIS samples submitted for Cr₆₊ analysis, and relying instead on the DUIS Cr₆₊ result to represent the mean DU concentration.

4.0 FIELD ACTIVITIES

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The field activities for this sampling event include reconnaissance of the farm fields and residential yards, collection of locational data, collection of discrete and incremental surface soil samples from within each SU, collection of residential well samples, and documenting these activities in a field book, on field sheets, and with photographs. Samples will be processed and analyzed for total Cr in the field, and returned to the HWP ESP laboratory for further processing before being subcontracted to another laboratory(s) for Cr₆₊ analysis.

4.1 Residential Yard Soil Sampling

4.1.1 Division of Yard into SUs

Staff will create a site sketch of each property noting magnetic north, buildings and other permanent structures, such as residences, and their orientation to the road, and the road's identity. Any obvious boundaries to the yard will be noted on the field sketch, e.g. fences, tree line, etc. Apparent children's play areas will also be included on the sketch. A photograph will be taken of each residence/yard, and a GPS point will be collected from near the main entrance to the residence.

The property will then be divided into sampling units based on field observations, with the residence (or other structures if applicable) generally considered as the reference point for the sampling units. Depending on the size of the lot and layout of the property, three to six sampling units will be established using guidelines in the EPA Superfund Residential Lead Sites Handbook (EPA, 2003). The Yard sampling units will generally not extend beyond 200 feet from the residential structure, and will be confined by property boundaries, fences, or other obvious barriers observed within the 200 foot distance limit. However, if an obvious high use area is observed beyond the 200-foot radius limit, it may be sampled as part of the yard. The focus will be on sampling primarily in areas where potential residential exposure may occur.

The orientation of the sampling units will be noted on the site sketch. Each sampling unit boundary will be traced on the field sheet in permanent marker and labeled, e.g. Y1, Y2, etc. A single set of GPS coordinates will be determined for each residence, taken at the center point of sampling unit Y1

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which will generally be located to the right and in front of the residence as it viewed from the road. The coordinates will be recorded on the field sheet.

4.1.2 Collection of Yard Soil Samples

Within each SU, staff will collect an incremental sample consisting of equal-mass aliquots of surface soil (0-2") from equally-spaced locations within the SU. Any vegetation, rocks, or other non-soil debris will be removed, and the surface (0-2") will be loosened and mixed in place. Where dense sod or other vegetative layer is present, a sampling spoon or trowel will be used to peel back the vegetation, which will then be shaken over the exposed area to release soil bound in the roots. A stainless steel spoon will then be used to collect approximately 100g of soil at each aliquot location. Each SUIIS sample should contain enough bulk soil to yield at least 200g of dried/sieved soil after processing.

The samples will be entered onto a COC in the field, and sample label tags will be placed on the bags. The Location ID will be entered into the Sample Reference field on back of the COC form, and the parcel number and sampling unit will be entered in the Comments field. Each sample bag will also be labeled with this information, plus date and time collected using permanent marker directly on the bag in case the sample tag comes off.

4.1.3 Collection of Private Well Samples

Samples will be collected from taps nearest the well heads. A GPS point will be collected at the wellhead or as near to it as practical. After opening the tap at a high flow for approximately five minutes, the field parameters temperature, specific conductivity (spec. cond.), oxidation reduction potential (ORP), and pH will be measured. A second set of measurements will be collected at 3 minutes. If the two measurements of temperature, conductivity and ORP vary by less than 10% and pH varies by less than 0.2, laboratory samples will be collected. If the measurements vary by greater than 10% and 0.2 for pH, additional measurements will be taken every minute until the parameters stabilize. Three 250ml HDPE sample containers will be filled at each well sampled. Sample containers will be filled directly from the taps at a low flow. Two containers will be field filtered through a 0.45 micron filter. One bottle will be preserved by adjusting the pH to >9 with a buffer

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Sampling and Analysis Plan

solution consisting of ammonium sulfate and ammonium hydroxide for Cr⁶⁺ analysis as specified in EPA Method 7199. The other filtered sample bottle will be adjusting to pH <2 with HNO₃ for dissolved Cr analysis. The unfiltered sample container will be preserved with HNO₃ to a pH < 2 and submitted for total Cr analysis.

4.2 Farm Field Sampling

4.2.1 Establishing DUs and SUs

Arial photography of each of the 15 selected farm fields will be overlain with a numbered grid of 1-acre SU cells using GIS prior to mobilization. If the field is significantly greater than 80-acres, it will be divided evenly into 2 or more DUs. The photo with grid overlay will be downloaded to hand-held GPS units for navigation in the field. Once in the field, staff will conduct reconnaissance to select 5 separate areas within the field to use as the initial SUs for sampling as described in Section 3.10.1. The 5 SUs will be marked using flagging in the corners to identify them for subsequent sampling.

4.2.2 Determining Increments/Sample and SUs/DU

Staff will navigate to 3 of the 5 SUs and collect 10 evenly spaced discrete surface soil samples into Ziploc baggies using stainless steel spoons. The samples will be minimally prepared prior to sample collection. Any vegetation, rocks, or other non-soil debris will be removed, and the surface (0-2") will be loosened and mixed in place. Each sample will consist of approximately 30-100g of soil. The parcel #, Location ID, and SU # will be written on the bag in permanent marker.

The samples will be transported to an on-site mobile laboratory. If soil conditions are amenable, the samples will be disaggregated with mortar and pestle, homogenized, passed through a #60 sieve, and returned to the bag. A larger mesh size sieve (e.g. #10 or #30) may be used if soil conditions do not allow enough material to pass through the #60 sieve. If soil moisture prevents sieving in the field, the samples will be dried on-site using a convection toaster oven to a moisture level that allows homogenization and sieving.

Tannery Sludge Farm Fields and Residential Yards
Sampling and Analysis Plan

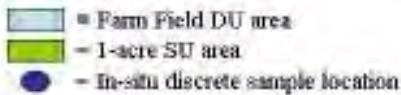
The homogenized/sieved samples will be analyzed for total Cr using benchtop XRF in accordance with the SOP in Appendix C. Each sample bag will be analyzed 4 times and the results averaged. A standard reference material (SRM) will be identified having a similar concentration of Cr as the bagged sample. The variability (as standard deviation) of the XRF readings on that SRM will be used as the QC acceptance criteria for the sieved yard sample homogeneity. The SD of the 4 replicate bag analyses will be compared to the SD of the SRM. If the SD of the yard sample replicates is within 3 times the SD of the SRM, the sample will be considered homogenous. If the criteria are not met, but is close, 4 additional XRF analyses will be conducted on the bag, and the comparison repeated on the 8 analyses. If the bag still fails, any procedural weakness in the sample preparation will be identified and rectified (e.g. disaggregate again, re-sieve, etc.).

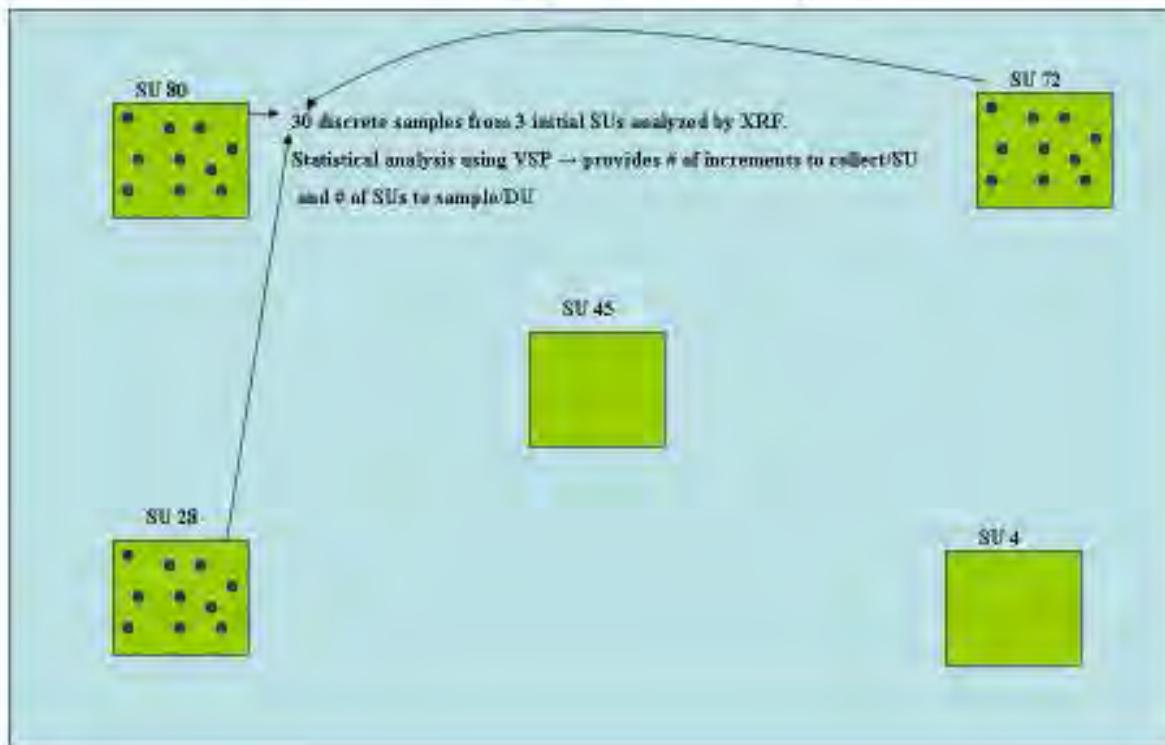
For each SU, the mean and SD of the 10 results will be calculated. The within-SU mean and SD values for the 3 SUs will be entered into Visual Sample Plan (VSP) to calculate the number of samples (increments) needed to demonstrate that the true SU mean is below the screening level with 95% confidence (PNL, 2009). VSP also requires input for the width of the grey region (difference between the mean and the screening level), which will be determined using an adjusted screening level calculated by multiplying the Cr₆₊ screening level of 86 mg/kg by the maximum observed ratio of Cr_{6+:}Cr from the pilot study. As a conservative measure, the VSP result from the SU that generates the highest number of required increments will be used for all SUs subsequently sampled for that DU. This value will represent the number of pooled increments that will be collected within each SU for samples being submitted for Cr₆₊ analyses.

The 3 SU means will then be used to calculate a DU mean and SD, and those results will be entered into VSP to determine the number of one-acre SUs that would need to be sampled within the field to demonstrate that the true DU mean is below the screening level with 95% confidence. This first portion of the sampling design is shown graphically in the following figure.

Tannery Sludge Farm Fields and Residential Yards
Sampling and Analysis Plan

Farm Field Design Step 1





4.2.3 Collection of SUIS and DUIS Samples

Staff will then return to the field and collect the SU samples for Cr⁶⁺ analyses. Samples will be collected in the determined number of SUs, collecting a single sample within each SU consisting of the number of determined increments. However, as a conservative measure, regardless of the outcome of the VSP analysis, a minimum of 5 SUs will be sampled at each DU, and a minimum of 10 increments will be collected per SU sample. The increments will be collected in the same manner as the 10 discrete samples from each SU, but they will be combined together into one large Ziploc bag. Note that once the XRF analysis is completed, the discrete samples collected from the initial 3 SUs can be combined together to create IS for those SUs. However, if it is determined that more than 10 increments are needed per SU, staff will return to those SUs and collect the additional increments. The mass of soil to be collected per SUIS sample will be estimated in the field based on the need to provide

Tannery Sludge Farm Fields and Residential Yards
Sampling and Analysis Plan

at least 200g of soil per sample for laboratory analysis after the sample is dried and passed through a #60 sieve. An adhesive sample tag will be filled out completely and placed on each SUIS. The Parcel #, Location ID and SU number will also be written on each SUIS sample bag in permanent marker.

4.3 Field Sample Identification

A unique 3-digit location ID will be assigned to each residential or farm field DU prior to mobilizing. Each DU will be associated with a parcel ID that corresponds to the farm field parcel number from the County Tax Assessor. Since a given parcel number can be divided into more than one farm field DU, and have more than one residence adjacent to it, multiple location IDs can be associated with each parcel. Samples will be identified with the location ID, parcel ID, sampling unit designation (SU, DU, or GW), and number for the SU taken from the GPS grid overlay. Each soil sample bag will contain the Parcel ID, Location ID, and SU designation, date and time collected written on the bag in permanent marker. The following provides an example of the sample identification scheme for a hypothetical farm field that is divided into two DUs with two adjacent residences (note that most parcels will only include one field DU and one residence DU).

Samples Associated with Hypothetical Parcel 130

First Farm Field DU - Location ID 101

Discrete samples for XRF analysis (SU#s are from pre-determined from grid cells)

SU20.1, SU20.2, SU20.3, SU20.4, SU20.5, SU20.6, SU20.7, SU20.8, SU20.9, SU20.10

SU48.1, SU48.2, SU48.3, SU48.4, SU48.5, SU48.6, SU48.7, SU48.8, SU48.9, SU48.10

SU61.1, SU61.2, SU61.3, SU61.4, SU61.5, SU61.6, SU61.7, SU61.8, SU61.9, SU61.10

Incremental samples

SU20IS, SU48IS, SU61IS, SU70IS, SU14IS, DUIS (triplicate IS samples will be denoted using a lower case letter, e.g. SU20ISa, SU20ISb, SU20ISc). When splitting IS samples into 3 aliquots, designate with a decimal and number, e.g. SU20IS.1, SU20IS.2, SU20IS.3)

Second Farm Field DU - Location ID 102

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Sampling and Analysis Plan

Discrete and IS sample designation is the same as above, except for the different location ID and different SU numbers corresponding to those grid cells selected for sampling in DU2.

First Residence - Location ID 103

Incremental samples

Y1IS, Y2IS, Y3IS, Y4IS, DUIS (triplicate IS samples denoted with lower case letter, e.g. Y1ISa, b, c)

Private well sample

GW

Second Residence - Location ID 104

Same as above, except for the different Location ID

Each sample will be entered on COC forms. The Location ID written in the Sample Reference field, and the Parcel ID and sampling unit designations will be written in the comments field.

4.4 Sample Preparation

The SUIIS samples from both the yards and the fields will be processed by drying to a moisture content of < 20%, disaggregating with a mortar and pestle, and passing through a #60 sieve. This may be done either in the field if the samples are already dry, or later at the ESP laboratory. The mortar and pestle and sieve pan will be cleaned with Simple Green detergent and rinsed with DI water between samples, and the sieve mesh will be decontaminated using a bristle brush, and damp paper towel. Since the yard pilot study indicated that the yard samples cannot be assessed for homogeneity using total Cr XRF analyses due to sensitivity limitations, they will be further homogenized by passing the sieved sample repeatedly back through a #30 sieve to provide additional mixing.

The sieved farm field samples will be assessed for homogeneity by analyzing each dried and sieved SUIIS soil sample 4 times by XRF, moving the sample bag between each analysis. A standard reference material (SRM) will be identified having a similar concentration of Cr as the bagged sample. The variability (as standard deviation) of the XRF readings on that SRM will be used as the QC acceptance criteria for the sieved yard sample homogeneity. The SD of the 4 replicate bag analyses

Tannery Sludge Farm Fields and Residential Yards
Sampling and Analysis Plan

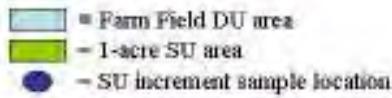
will be compared to the SD of the SRM. If the SD of the yard sample replicates is within 3 times the SD of the SRM, sample processing will continue as described below. If the criteria are not met, but is close, 4 additional XRF analyses will be conducted on the bag, and the comparison repeated on the 8 analyses. If the bag still fails, any procedural weakness in the sample preparation will be identified and rectified (e.g. disaggregate again, re-sieve, etc.).

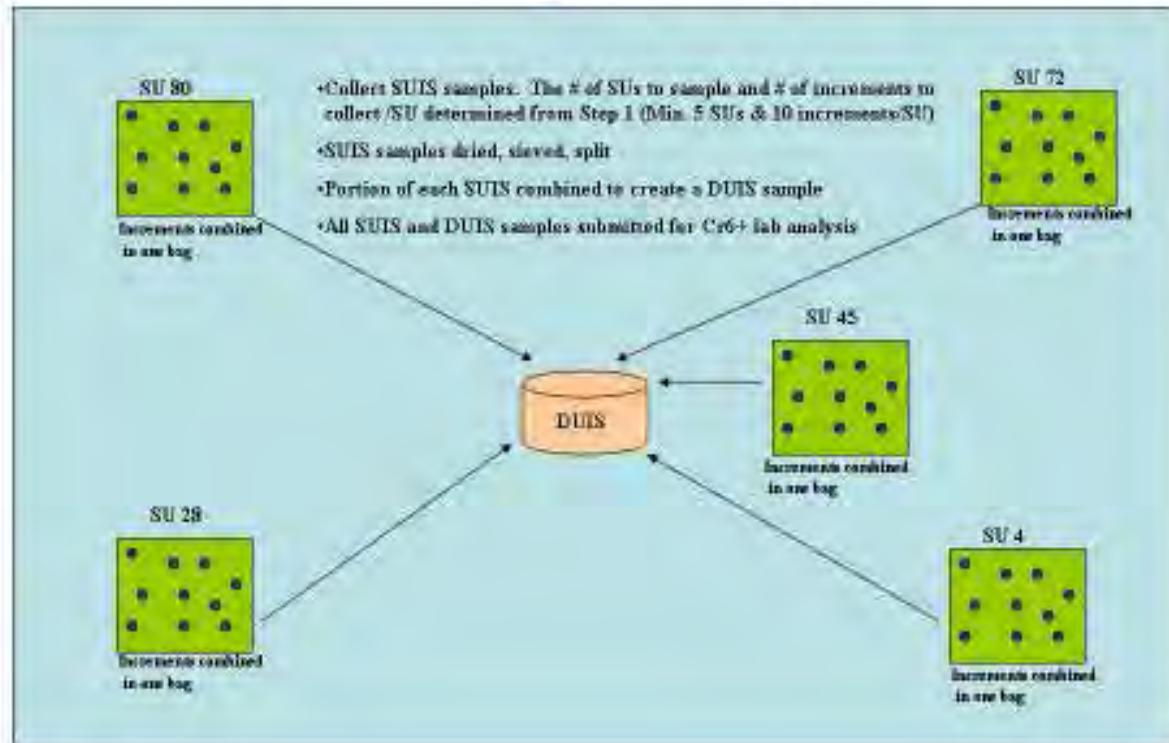
Once each SUIS sample is shown to be homogenous, it will then be split into 3 equal portions. One aliquot will be placed in an 8 oz glass jar and sent to a contract laboratory for Cr₆₊, pH, Eh, and TOC analyses, one will be combined with aliquots from the other SUIS samples to create a DUIS which will also be sent for those same analyses, and the third aliquot will be submitted to the ESP CAS lab for analysis of Al, Fe, Mn, Mo, and V. Following division of the farm field SUIS samples, each of the three aliquots will be analyzed for total Cr by XRF to demonstrate that they were representatively split. The splits will be analyzed 4 times by XRF. The splits will be considered representative of the original SUIS sample if the means are within the 95% confidence interval of the pre-split sample (using 2-sided t-value). If the criteria is not met, but is close, 4 additional XRF analyses will be conducted on the bag, and the comparison repeated on the 8 analyses. If the bag still fails, any procedural weakness in the sample preparation will be identified and rectified (e.g. re-sieve, etc.).

Once the homogeneity and representativeness of the farm field SUIS sample splits has been demonstrated, the yard and farm field DUIS samples will be created by combining equal-mass aliquots of SUIS samples together. The DUIS sample mass should be a minimum of 200g. The design for Collection of SUIS and DUIS samples is shown graphically in the following figure.

Tannery Sludge Farm Fields and Residential Yards
Sampling and Analysis Plan

Farm Field Design Step 2





4.5 Sample Quantity and Laboratory Analysis

The number of soil samples collected will depend upon the number SUs identified for sampling in each farm field and residence. We anticipate 22 farm field DUs (incl. backgrounds) with 5-10 SUs per DU, and 12 residential DUs (incl. backgrounds) with 4-6 SUs per residence. We anticipate that each residence will have a private drinking water well. Based on these estimates, and accounting for QC samples, a range of 156-288 soil samples will be collected from the farm fields and, 60-84 soil samples from the residential yards including QC samples. Sample numbers, analyses, sensitivity requirements, sample preservation, and holding times are summarized in the following tables.

**Tannery Sludge Farm Fields and Residential Yards
Sampling and Analysis Plan**

Dried & Sieved Surface Soil Samples

Analyte/Method	Minimum Volume (g)	Sensitivity Requirements	Sample Container	Preservative	Holding Time	Estimated Number of Samples
Cr6+/EPA SW-846 Method 3060a/7199	100	2 mg/kg	8 oz glass jar	Cool, 4°C	30 days	156-288
Cr6+/EPA SW-846 Method 3060a/7199	100	0.2 mg/kg	8 oz glass jar	Cool, 4°C	30 days	60-84
Total Fe, Mn, Mo, V, Al / EPA SW-846 Method 6010	10	10 mg/kg	8 oz glass jar	Cool, 4°C	6 months	156-288
Total Organic Carbon/ ASTM Method D2974	50	NA	8 oz glass jar	Cool, 4°C	30 days	156-288
Redox Potential / SW-846 Method 9045	20	NA	8 oz glass jar	Cool, 4°C	30 days	156-288
pH / SW-846 Method 9045	20	NA	8 oz glass jar	Cool, 4°C	30 days	156-288

Private Well Water Samples

Analyte/Method	Minimum Volume (ml)	Sensitivity Requirements	Sample Container	Preservative	Holding Time	Estimated Number of Samples
Cr6+/EPA Method 218.6	10	0.05 ug/L	250ml HDPE plastic	pH 9-9.5 with buffer soln.	24 hours	12
Total and dissolved Cr/EPA Method 200.8	100	10.0 ug/L	250ml HDPE #2 plastic	HNO3 to pH<2	6 months	12

Results for redox potential and TOC on the farm fields soil samples will be evaluated after the first analyses are completed. If no significant correlation is found between these parameters and the ratio of

Tannery Sludge Farm Fields and Residential Yards Sampling and Analysis Plan

Cr₆₊:Cr, further analyses for these parameters may be dropped to save on analytical costs. Laboratory duplicates will be requested at a frequency 10% for soil samples submitted for Cr₆₊ analysis. Lab duplicates and matrix spikes performed by the laboratory for Cr₆₊ analysis will be done on MDNR samples regardless of other samples in the analytical batch.

The following QC data will be requested from the laboratory performing the Cr₆₊ water and soil analyses in order to conduct uncertainty analysis on the results:

- Instrument calibration standards with "as made" & "as reported" after calibration values. Ex:
If there are 4 calibrators with the following "as made" concentrations: 10.0, 50.0, 100.0 and 200.0, than at least 20 observations are required, so for this example 5 sets would be requested (data from the last 5 calibration runs). If there are 5 calibrators in the curve, then only 4 recent sets would be requested.
- At least 20 recent results for a continuing calibration verification standard and the std's stated value
- At least 20 recent results for a second source QCS (quality control sample, sometimes called laboratory control sample) and its stated/expected value
- At least 20 recent results for matrix spikes with actual and expected values

4.6 Laboratory Subsampling

Soil samples submitted to the laboratory for Cr₆₊ analysis will be subsampled using the 2D Japanese Slabcake technique. The entire sample will be spread evenly onto a 2 dimensional surface at a depth that can be easily penetrated by a scoop. A scoop will then taken by removing an increment that equally represents the entire vertical column of the material and placed in a receiving container. This process is repeated at least 30 times at random locations around the entire sample. A square walled scoop tends to perform the best. Each scoop will ideally represent 1/30th of the desired target mass. For example, with an analytical method that requires a 2.5 gram sample to be digested, each scoop should weigh about 83.5 mg (83.5x 30=2,500mg). Before starting the scooping process, a few trial

Tannery Sludge Farm Fields and Residential Yards Sampling and Analysis Plan

scoops should be taken and weighed, to calibrate the amount needed for each scoop. This process is repeated on samples identified as laboratory duplicates.

4.7 Chain of Custody

All samples collected during the investigation shall remain in the custody of HWP and/or ESP personnel in the field, and will be stored and transported in coolers on ice. Aqueous samples for Cr₆₊ analysis will be next-day shipped from the field directly to the laboratory the day they are collected. Aqueous samples for other analyses will be relinquished to a sample custodian at the state's environmental laboratory within the ESP in Jefferson City for analyses. Non-aqueous samples will remain in the custody of ESP personnel during sample preparation and be relinquished to HWP personnel for XRF analysis. Following XRF analysis, non-aqueous samples to be submitted for laboratory analyses will be relinquishing to a sample custodian at ESP in Jefferson City for analysis by CAS or shipment to an outside lab for Cr₆₊ analysis.

5.0 QUALITY CONTROL

5.1 Field Methods

Clean disposable nitrile gloves will be worn by sampling personnel. Field personnel shall note all observations, sample locations, and descriptions on a standardized field sheet. ESP will note their observations and measurements in personal field notebooks. Standard Operating Procedures (SOPs) will be followed in the field during sample collection (MDNR-ESP-001, -002, -003, -004, -005, -007)

5.2 Field Decontamination

A clean sample bag and spoon will be used for each sample collected. Spoons used to collect soil samples will be disposable, and do not require field decontamination.

The mortar/pestle, sieves and sieve collection pans will be decontaminated between each sample using a small bristle brush followed by wiping with a damp paper towel. A clean reference soil material will be processed through the mortar/pestle and sieve following sample processing initially to demonstrate there is no carryover of Cr between samples.

Tannery Sludge Farm Fields and Residential Yards Sampling and Analysis Plan

5.3 Precision

XRF precision will be assessed from replicate analyses conducted on selected soil sample bags (without moving the bag between analyses) at a frequency of 5% or one set per day minimum. The %RSD between 7 replicate analysis conducted on the sample bag should be less than 15%.

Laboratory duplicates will be requested on samples submitted for Cr₆₊ analyses at a frequency of 10% and used to assess lab subsampling and Cr₆₊ analytical precision. Laboratory precision will also be assessed from the analysis of matrix spike/spike duplicates.

The overall precision of sampling and analysis will be assessed using replicate SUIs samples. At 5%-10% of the SUs sampled, triplicate incremental samples will be collected, processed and analyzed for Cr₆₊.

5.5 Accuracy

The accuracy of XRF analyses will be assessed by the routine analysis of standard reference materials containing certified concentrations of chromium. The results of the SRMs analyses will be compared to control charts. The XRF's internal calibration and standardization routines will be considered valid if the measured values are within +/- 2 standard deviations of the control chart mean.

Laboratory accuracy will be assessed using instrument calibration standards, continuing calibration verification, and matrix spike analyses as specified in the analytical methods.

5.6 Representativeness

Sample representativeness is the ability of a sample to represent the average concentration over a defined sampling unit in the context of the decision to be made on that sampling unit. Representativeness is a function of sample numbers/density across an area of interest, and sample support and sample processing that maintains the representativeness of the sample through the series of subsampling events needed to get to the analytical sample.

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In this project, representativeness is maximized by using composite/incremental sampling to increase sampling density. The sampling density is being matched to statistical measurement of spatial heterogeneity in the field.

Whether representativeness has been achieved will be determined by comparing the degree of matching between composite samples and the statistical confidence interval calculated from the increment results composing the IS. If the composite mean is within the confidence interval of the component results, then the representativeness criterion is met for field sampling, and will be assumed to be met for any subsequent sampling in that unit area.

For subsampling, representative sample processing and subsampling is determined as described in section 4.4. Section 4.6 discusses the lab subsampling procedures to be used to minimize the effect of matrix heterogeneity to maximize the representativeness of the analytical sample.

Section 4.5 discusses the water preservation techniques to be used to ensure that the Cr₆₊ concentration remains representative of field conditions during sample holding times.

5.7 Completeness

Completeness refers to having enough data to support a decision at the desired level of confidence. For this project, statistical evaluation of the data must show 95% confidence before a decision of “clean” can be made. Real-time statistical evaluation of the XRF total Cr data is used to predict that a complete Cr₆₊ data set will be available when Cr₆₊ results are returned from the laboratory.

6.0 INVESTIGATION DERIVED WASTES (IDW) PLAN

Efforts will be made to minimize IDW generation. IDW may include soils, disposable sampling equipment, and disposable personal protective equipment (PPE).

**Tannery Sludge Farm Fields and Residential Yards
Sampling and Analysis Plan**

Field personnel will return unused soils to their source immediately after generation. Disposable PPE and disposable sampling equipment will be handled as solid waste, containerized, and properly disposed.

7.0 SITE SAFETY

A health and safety plan will be generated prior to field mobilization, indicating appropriate emergency contact numbers and safety considerations.

A safety briefing will be held on-site prior to initiating field activities and field personnel will be required to read and sign the site-specific health and safety plan. A copy of the health and safety plan will be available on-site for reference. The site safety plan is attached as Appendix B.

8.0 REPORTING

The analytical results, associated QC data, field notes, COC forms will be submitted to the HWP. The HWP project manager will prepare a project report.

Tannery Sludge Farm Fields and Residential Yards Sampling and Analysis Plan

Prepared by:

Michael Stroh
Environmental Specialist
Superfund/Site Assessment Unit
Hazardous Waste Program

Reviewed by:

Ken Hannon
Ken Hannon
Environmental Specialist
Field Services Section
Environmental Services Program

Approved by:

Julieann Warren
Julieann Warren
QA Officer
Hazardous Waste Program

Date:

1/14/10

To be signed by all staff participating in the sampling event:

“I have read and understand the Sampling and Analysis Plan”

Name:

Date

Tannery Sludge Farm Fields and Residential Yards
Sampling and Analysis Plan

9.0 REFERENCES

DHSS, 2009 Baysinger, Cherri, Missouri Department of Health and Senior Services, to Dennis Stinson, MDNR Hazardous Waste Program, Letter Re: DHSS Recommendation for a Screening Level For Hexavalent Chromium in Drinking Water for the Tannery Sludge Farm Fields Site, December 17, 2009, 3 pages.

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APPENDIX A
FIGURES

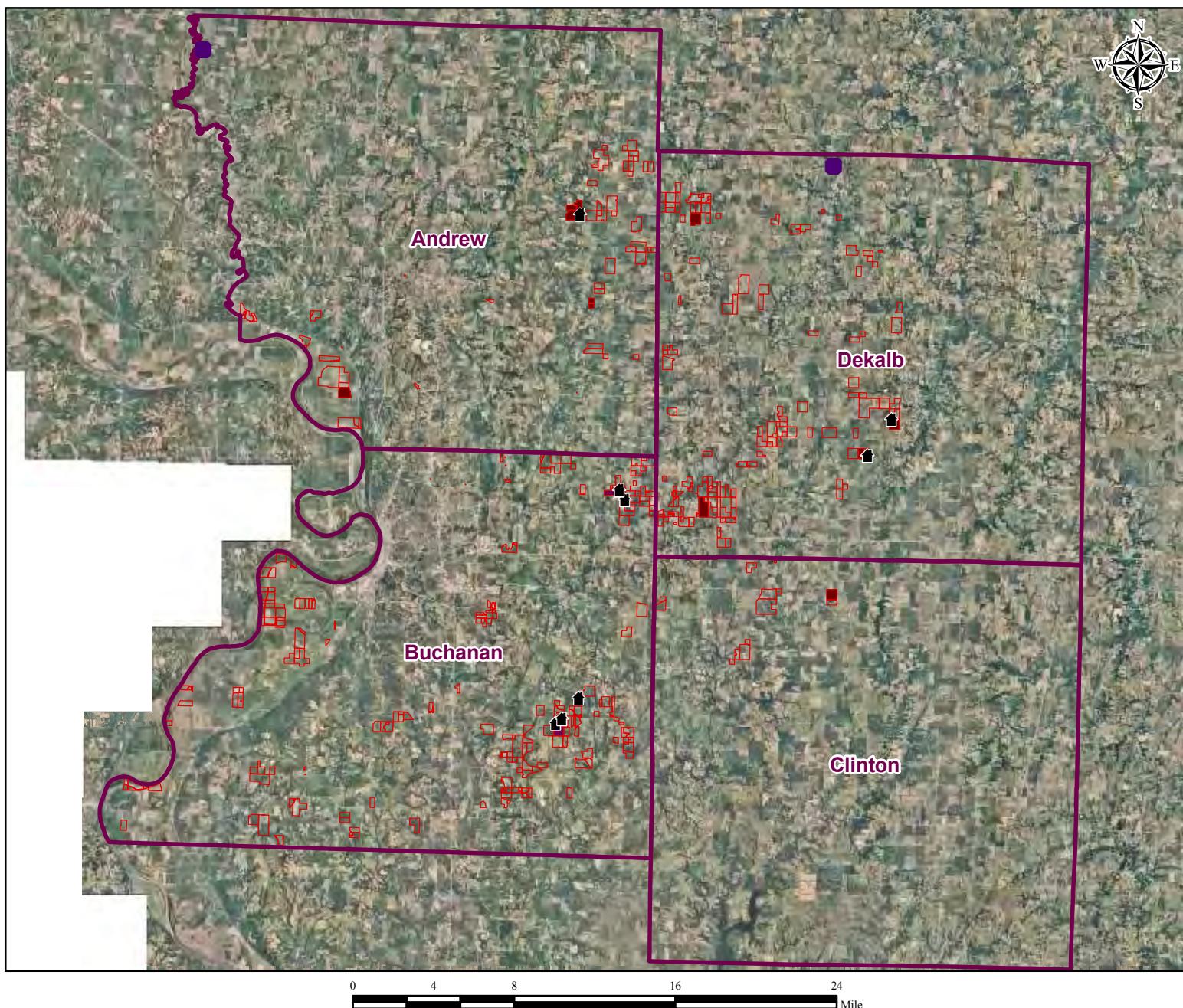


Figure 1: Proposed Sample Location Map
As of November 24, 2009
Tannery Sludge Farm Fields Site
Andrew, Buchanan, Clinton and Dekalb Counties
Missouri



APPENDIX B

HEALTH AND SAFETY PLAN

**MISSOURI DEPARTMENT OF NATURAL RESOURCES
DIVISION OF ENVIRONMENTAL QUALITY
ENVIRONMENTAL SERVICES PROGRAM**

**Tannery Sludge Farm Fields Site
SITE HEALTH AND SAFETY PLAN**

1.0 INTRODUCTION

This plan has been prepared for implementation by ESP employees, using operating procedures for which they are specifically trained. Any use of the plan by other agencies, organizations, or private individuals is at their own risk.

2.0 KEY PERSONNEL

MDNR OSC: Michael Stroh SAFETY OFFICER: Kenneth Hannon

OTHER MDNR PERSONNEL/TITLE:

Pam Hackler ES III – ESP Ben Frissel ES III - ESP

Sean Counihan ES III – ESP Valerie Wilder ES III - HWP

Brad Swank ES III – ESP Shelly Jackson ES III - HWP

3.0 SITE INFORMATION

Site name Tannery Sludge Farm Fields Site

County/City: Andrew, Buchanan, Clinton, Dekalb

Sampling date: 12/14/09 Site Description: Fields where tannery sludge was applied.

3.1 Overall Incident Risk/Hazard Analysis

Chemical: Serious Moderate XX Low Unknown

Physical: Serious Moderate XX Low Unknown

3.2 Contaminant(s) of Concern: Hexavalent chromium and potential contaminants from tanning industry.

3.2.1 Physical State: XX Liquid XX Solid XX Sludge Gas/Vapor

Chemical Characteristics: (check all that apply)/

XX a. carcinogen b. biological c. corrosive d. combustible
 e. explosive f. flammable g. volatile h. poison
 i. radioactive j. reactive k. other: _____

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SITE HEALTH & SAFETY PLAN
PAGE 2

3.2.2 Physical Hazards: (check all that apply)

a. overhead b. below grade c. confined space* d. noise
 e. splash f. fire/burn g. puncture h. heat stress
 i. cut j. slip/trip/fall k. cold stress l. electrical
 m. mechanical/heavy equipment n. other: _____

* The need for confined space entry by ESP personnel shall be evaluated on a site-by-site basis. A confined space entry permit must be signed by the appropriate Unit or Section Chief prior to ESP employees entering a confined space (29 CFR 1910.146). Confined space entry shall be screened in at least Level B prior to downgrade. **Adequate resources must be available and specific planning and tasks determined before confined space entry is initiated.**

3.3 Task-Specific Risk Analysis (attach additional sheets as necessary)

Task Description	Chemical Hazards	Physical Hazards	Level of Protection
Water sample collection	a h	i j	D
Soil/sludge sample collection	a h	e i j	D

4.0 MEDICAL SURVEILLANCE AND PERSONNEL TRAINING REQUIREMENTS

All ESP field personnel participate in a medical monitoring program and are trained at least to the level of "Hazardous Substance Emergency Response-Technician" as required and specified in the department's written health and safety program located in Section 2 of the MDNR-Hazardous Substances Emergency Response Plan (HSERP). The written policy satisfies requirements set out in 29 CFR 1910.120. MDNR ESP's respiratory protection program meets the requirements of 29 CFR 1910.134.

ESP personnel will ascertain as much information as possible regarding health and safety issues associated with the site prior to initial entry. Information shall include chemical and physical hazards as listed above, types and amounts of materials involved, and citizens/areas threatened by the incident.

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SITE HEALTH & SAFETY PLAN
PAGE 3

5.0 PERSONAL PROTECTIVE EQUIPMENT

ESP shall utilize the Protection Level categories defined in 29 CFR 1910.120, Appendix B, and known as Levels A, B, C, and D. Refer to Section 2 of the MDNR-HSERP for definitions of Protection Levels. ESP personnel shall inspect APRs and SCBAs at least monthly and maintain a record of such to ensure equipment is functional.

Levels of protection shall be reassessed and upgraded as conditions change and information is updated to comply with worker safety while performing site activities.

Action Levels for evacuation of work zone pending reassessment of conditions:

Level D: O₂ < 19.5% or > 25%; explosive atmosphere > 10% LEL; organic vapors > background levels;
other _____.

Level C: O₂ < 19.5% or > 25%; explosive atmosphere > 10% LEL; organic vapors (in breathing zone) > 25 m.u., or 3 times background (whichever is less); other _____.

Level B: Explosive atmosphere > 10% LEL; unknown organic vapors (in breathing zone) > 500 m.u.;
other _____.

Level A: ESP personnel shall evaluate the need for entry on a site-specific basis and may utilize its emergency response contractor for Level A situations which may arise.

6.0 FREQUENCY AND TYPE OF AIR MONITORING/SAMPLING

Instrument	Contaminant of Concern	Sample Location (Area/Source)	Frequency	Odor Threshold/ Description
N/A				

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SITE HEALTH & SAFETY PLAN
PAGE 4

7.0 SITE CONTROL MEASURES

7.1 The "Buddy-System": ESP personnel performing any work activities within the exclusion zone shall employ the "buddy-system" at all times, as required and defined in Section 2 of the MDNR-HSERP. The "buddy-system" may not be required while an ESP staff member is observing or providing oversight of cleanup activities performed by a contractor or responsible party.

7.2 Safe work Practices: Refer to Section 2 of the MDNR-HSERP for written safety practices to be followed at all times by ESP personnel while on-site at an incident.

7.3 Site Communications: The use of two-way radios or establishment of hand signals for communications shall be determined prior to entering the work zone and followed by ESP personnel.

7.4 Work Zones: ESP personnel shall ensure work zones are established and be aware of their locations.

8.0 DECONTAMINATION PROCEDURE/SOLUTIONS:

Personnel: Soap/water wash all skin exposed to potentially contaminated media

Equipment: Refer to Equipment decontamination procedures specified in the site specific sampling plan.

Instruments: _____

Decontamination fluids/materials may be to be containerized for proper disposal.

9.0 EMERGENCY INFORMATION:

In the event of an emergency, notify the MDNR Environmental Emergency Response Office at 573/634-2436. The Duty Officer will make the appropriate notifications.

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10.0 ADDITIONAL EMERGENCY INFORMATION/NUMBERS:

Hospital: South Side Health Center – 5001 Lake Avenue., St. Joseph, MO –816/238-7788

Location/Specific directions from Site: Refer to attached map

	<u>Name/Location</u>	<u>Telephone Number</u>
Ambulance:	<u>St. Joseph Ambulance</u>	<u>911</u>
Police/Sheriff:	<u>St. Joseph Department</u>	<u>911</u>
Fire:	<u>St. Joseph Department</u>	<u>911</u>
Poison Control:		
Cellular Telephones/Other:	<u>Ken Hannon digital phone:</u>	<u>573/644-3217</u>

11.0 SIGNATURES

ESP personnel shall certify they have read the plan and addressed any questions regarding worker health and safety by signing and dating below followed by printing their name and title.

Signature

Printed Name/Title

Date

TLD Badge

APPENDIX C

XRF STANDARD OPERATING PROCEDURE

Standard Operating Procedure for Innov-X α 400sl XRF Analyzers

Tannery Sludge Farm Fields and Residential Yards Project

The instruments will be operated in the testing stand and controlled from a laptop PC. A 180-second or 100-second analysis time will be used for all samples depending on Cr concentration range. *Note, do not operate the laptop PC software with the laptop connected to the network servers.*

All XRF analyses will be recorded in a written log book for each instrument. The analyst will record the date, the XRF run number (automatically generated by the XRF), the sample ID, and the total Cr result in mg/kg.

Startup

- Power up the analyzer, allow to warm up 15 minutes, then start the InnovX PC software.
- The instrument will automatically perform an initialization procedure, which lasts for 1-2 minutes.
- Following initialization, place the stainless steel standardization disc over the instrument's sampling window in the test stand and close the stand cover.
- Click the “Standardize” button from the upper left window titled “Soil” in the PC software. The instrument will perform an internal 60-second standardization procedure. During standardization, and any other time the x-ray tube is on, the red light on top of the test stand will flash. When the x-ray tube is off, the red light will remain on solid. **Do not open the test stand lid when the light is flashing.**
- Following standardization, an information window will pop up displaying the analyzer resolution. Record the resolution in the XRF Log Book along with the Run number automatically assigned by the analyzer.
- The analyzer is now ready to analyze standard reference materials (SRMs).

Calibration Check

- The NIST 2709, 3212, 4315, RTC408, 5861, and Blank SRMs will be analyzed at the beginning of each use.
- Place an SRM over the analyzer's sampling window, and close the testing stand cover.
- On the PC software main menu bar, select “Edit” and then chose “Edit Test Information”. A data entry window will pop up allowing input of information about the next test.
- Select your name from the “Analyst” dropdown menu & select the check sample from the “Chk_Smpl” dropdown list.
- Click OK, and set the analysis time: for SRMs blank, 2709, and 3212, use 180 seconds, for the other SRMs use 100 seconds.

- Click the “Start” button in the Soil Window in the upper left corner of the screen to initiate the test.
- Assess instrument calibration by comparing the measured values to the control chart for each SRM. Verify that the result is within 2SD of the control chart mean, if so, continue to Bagged Sample Analysis.
- If values outside 2SD are observed, re-analyze the calibration check sample. If the measured value is still outside 2SD, re-standardize as described above, and re-analyze the standard(s).
- A blank sand sample will be analyzed at least once per 20 samples, preferably following a high concentration sample.
- Re-check the calibration periodically throughout the day by analyzing the various SRMs and checking against the control chart.
- All the SRMs are analyzed again at the end of sample analysis and compared to the control chart.

Bagged Sample Analysis

- Following successful calibration check, click Edit from the main menu bar and select Edit Sample Information.
- Enter all applicable information about the first sample to be analyzed from the bag label, using the dropdown menus and direct edit fields
- Gently roll the sieved soil around inside the bag to homogenize;
- Place the sample over the analyzer’s sampling window ensuring that the soil and bag are in as close contact with the window as possible.
- Close the stand cover.
- Click the Start button from the Soil window to initiate the test.
- The data being acquired will appear in the Chemistry window in the lower center of the PC screen during analysis.
- The analysis will continue for 180 seconds unless stopped at 100 by the analyst. Analysis may be stopped at 100 sec if the concentration of Cr observed during the first 30 seconds is above 150 mg/kg.
- After analysis, the results will appear in the Results window on the PC.
- A running list of the analyses will appear in the window at the lower left of the PC screen.
- The sample information will remain from the previous test, so no changes are necessary for subsequent replicate analyses on a given sample bag.
- Roll the sieved soil around inside the bag, and re-analyze. Repeat analysis 4 times.

Refer to the SAP for guidance on how to assess the replicate bag readings. Data should be assessed and any additional analyses/measures taken before proceeding to the next bagged sample.

- After completing replicate analysis on a bagged sample, click the Edit Sample Information again and enter information for the next bagged sample as above.

- Place the second sample in the test stand, close the cover and initiate the analysis.
- Repeat for remaining samples
- An instrument precision check will be conducted at a frequency of 5%. This will consist of analyzing a sample seven separate times without moving the sample in between each analysis. The %RSD on the replicate analyses should not exceed 15%.

Daily Data Downloading

- After the last analysis for the day, select Readings from the main menu bar, and chose Export Readings.
- In the Export pop up box, verify that the “Export readings on date” radio button is selected, the Mode to export is “All”, and today’s date is circled on the calendar.
- Click OK.
- Insert a USB thumb drive in the laptop, download data to it, and then move data onto network server. Select the directory and file name for the downloaded data. For this project, file naming convention is date & XRF serial number (e.g. 12_14_09_5434)
- Verify that the file type is “Comma Separated Values”, and click Save.
- A message will pop up indicating a successful download, and asking whether you would like to open the file. Select Yes, and file will open in Excel. Verify that the data appears correct. Make any corrections you had noted in the run log book.
- Choose Save As from the File menu, and select File Type “Microsoft Excel 97 Workbook.”
- Close the InnovX software, power down the analyzer, and shut down the laptop PC.
- Copy the file from thumb drive to the network as soon as possible after analyses. Files will be stored in the H:/Sections/Superfund/SiteFiles/Tannery Sludge Fields/XRF data directory.

Note: For any operation that requests a password, the administrator password is lower case z, and the factory password is 1234.